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Fabrication of BiTeI submicrometer hollow spheres†

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BiTeI submicrometer hollow spheres with diameters of 200–300 nm have been synthesized by an iodine transport hydrothermal method without the use of template materials or surfactants. The preparation was carried out in an autoclave in the temperature range 190–200 °C with Bi_2Te_3 and I_2 as reactants. X-Ray powder diffraction patterns and transmission electron microscopy images show that the product is BiTeI with a hollow sphere structure. The sphere wall is composed of BiTeI nanoparticles with an average diameter of 5 nm and a thickness of *ca.* 10 nm. A possible growth mechanism for the hollow structure is proposed. The first excitonic peak of the BiTeI hollow spheres is considerably blue shifted in comparison with the band gap of the bulk material, which can be attributed to quantum confinement effects.

I Introduction

Semiconductor nanoparticles have some special characteristics due to their large surface-to-volume ratio, quantum size, and dielectric confinement effects.[1–6] Such nanoparticles are of both fundamental and technological interest due to the expectation that they may exhibit a variety of new spectroscopic features, including sharper absorption spectra, enhanced exciton and impurity binding energies, and modified electron–phonon coupling, which are very sensitive to both size and shape[7,8] Recently, the preparation and design of nanometer or submicrometer inorganic and hybrid hollow spheres[9–13] have received great attention because of the potential for new material properties and possible applications in a broad range of areas such as catalysis, coatings, composite materials, protecting sensitive agents such as enzymes and proteins, and electronics. Among these reported particles, CdS hollow spheres were the first example of an inorganic non-oxide semiconductor material with such a structure.[9,14] As far as we know, the hollow sphere structure is hitherto unknown for ternary V^{A}–VI^{A}–VII^{A} compounds.

Ternary semiconductor compounds of the type V^{A}–VI^{A}–VII^{A} have been extensively studied because of their unusual ferroelectric and photoelectric properties.[15] BiTeI, belonging to the V^{A}–VI^{A}–VII^{A} group of ternary compounds, is a p-type semiconductor with a 0.57 eV band gap.[16,17] BiTeI exhibits a 2H-CdI_2-type structure.[18] Each Bi atom is six-coordinated by three Te and three I atoms at distances of 3.88(5) and 3.05(2) Å, respectively, thus forming a distorted octahedron. The faces of the octahedron are two equilateral triangles (Te–Te–Te and I–I–I), with sides 4.336 Å in length, and six isosceles triangles (three I–Te–I and three Te–I–Te), with sides of 3.29(3) (I–Te) and 4.336 Å (I–I and Te–Te) in length.[19] Conventionally, BiTeI crystals are prepared by heating a stoichmetric mixture of BiI_3 and Bi_2Te_3 in an evacuated quartz tube to 650 °C for 4 h. Purification is acheived by sublimation under vacuum at 520 °C, followed by condensation at 455 °C for 3 days.[16–20] Recently, resonance tunneling and slow electron reflection spectra in layered BiTeI and BiTeBr semiconductors has been reported.[21]

In recent years, the chemical solution route has been emerging as one of many effective synthetic techniques for materials preparation.[22,23] The hydrothermal method is one of the most promising chemical solution routes due to its economy and the high degree of compositional control which can be acheived.[24] Our groups have developed hydrothermal methods for the preparation of many II–VI,[25] IV–VI_2,[26] and I–III–VI_2[27] materials, and $CdIn_2S_4$ nanocrystals.[28] On the basis of the above works, we have developed an iodine transport hydrothermal method.[29] In this study, we report a simple strategy for preparing BiTeI hollow spheres *ca.* 200 nm in diameter *via* an iodine transport hydrothermal route without the use of template materials or surfactants.

II Experimental

The chemical reaction we employed for synthesis of the BiTeI submicrometer hollow spheres can be formulated as shown in eqn. 1–3

$$I_2 + H_2O \rightarrow HI + HOI \tag{1}$$

$$2HOI \rightarrow I_2 + H_2O + 1/2O_2 \tag{2}$$

$$Bi_2Te_3 + 2HI \rightarrow 2BiTeI + H_2Te \tag{3}$$

In a typical procedure, Bi_2Te_3[30] and iodine (I_2) (molar ratio 1 : 6) were put into a Teflon-lined autoclave of 50 ml capacity. The autoclave was filled with distilled water up to 85% of the total volume and then maintained at 180–200 °C for 10 h, before being cooled to room temperature naturally. The products were filtered out and washed with distilled water several times. A black powder was obtained after drying under vacuum at 70 °C for 3 h.

The X-ray powder diffraction (XRD) pattern was obtained with a Rigaku Damax γA X-ray diffractometer with Cu-Kα radiation (λ = 1.54178 Å). The XPS spectra of the product were recorded on a VGESCALAB MK II X-ray photoelectron spectrometer, using non-monochromatized Mg-Kα radiation as the excitation source. Transmission electron microscopy

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†Electronic supplementary information (ESI) available: XRD pattern and TEM images of Bi_2Te_3. See http://www.rsc.org/suppdata/jm/b2/b200950c/

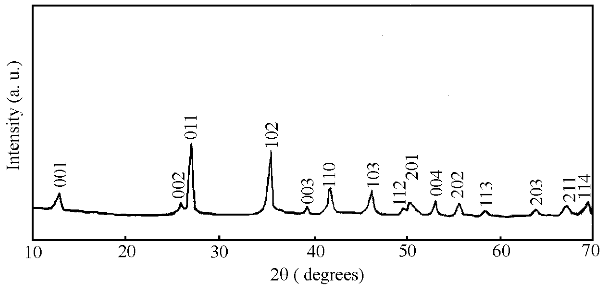

Fig. 1 XRD pattern of as-prepared BiTeI.

(TEM) images were obtained with a Hitachi H-800 transmission electron microscope, using an accelerating voltage of 200 kV. Samples for TEM were prepared by placing a drop of the sample suspended in absolute ethanol on a copper grid coated with carbon film and allowing it to dry in air. High resolution transmission electron microscopy (HRTEM) was carried out using a JEOL-2010 transmission electron microscope, employing an accelerating voltage of 200 kV. The UV-vis absorption spectra were measured at room temperature using a Shimadzu UV-240 spectrophotometer. The compositions of the samples were accurately analyzed using inductively coupled plasma-atomic emission spectroscopy (ICP-AES), using an Atomscan Advantage (Thermo Jarrell Ash Corporation) instrument.

III Results and discussion

Fig. 1 shows the XRD pattern of as-prepared BiTeI. All the reflections can be indexed to the hexagonal BiTeI phase, lattice constants $a = 4.344$ and $c = 6.912$ Å, values which are close to those reported for BiTeI (JCPDS Card File 43-650). No characteristic peaks due to other impurities were observed

The XPS spectrum of as-prepared BiTeI is shown in Fig. 2. The binding energies of Bi($4f_{7/2}$), Te($3d_{5/2}$), and I($3d_{5/2}$) were found to be 158.90, 576.25, and 616.05 eV, respectively. Quantification of the relevant XPS peaks gave a Bi : Te : I atomic ratio of 1 : 1.09 : 1.04, consistent with the expected values. Elemental analysis for the composition of the sample was measured by ICP-AES. The Bi : Te : I atomic ratio for BiTeI was found to be 1.000 : 0.993 : 1.082.

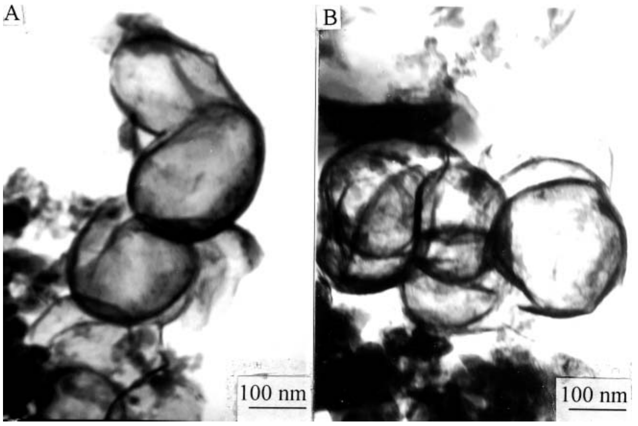

Fig. 3 TEM images of as-prepared BiTeI hollow spheres.

TEM images of as-prepared BiTeI are shown in Fig. 3. The sample consists of hollow spheres 200–300 nm in diameter. The wall thickness around the shell is estimated to be *ca.* 10 nm from the TEM images. The strong contrast between the dark edges and plate centers provides evidence of their hollow nature.[9,10,14b] The strongest proof that the as-prepared BiTeI spheres are hollow is the direct observation of a broken sphere, as shown in Fig. 4(A). Fig. 4(B) is an HRTEM image showing the structure of the BiTeI sphere wall. From this, it can be seen that the wall is composed of BiTeI nanoparticles, with an average diameter of 5 nm.

In our iodine transport hydrothermal route, the temperature and the amount of iodine are critical factors affecting the

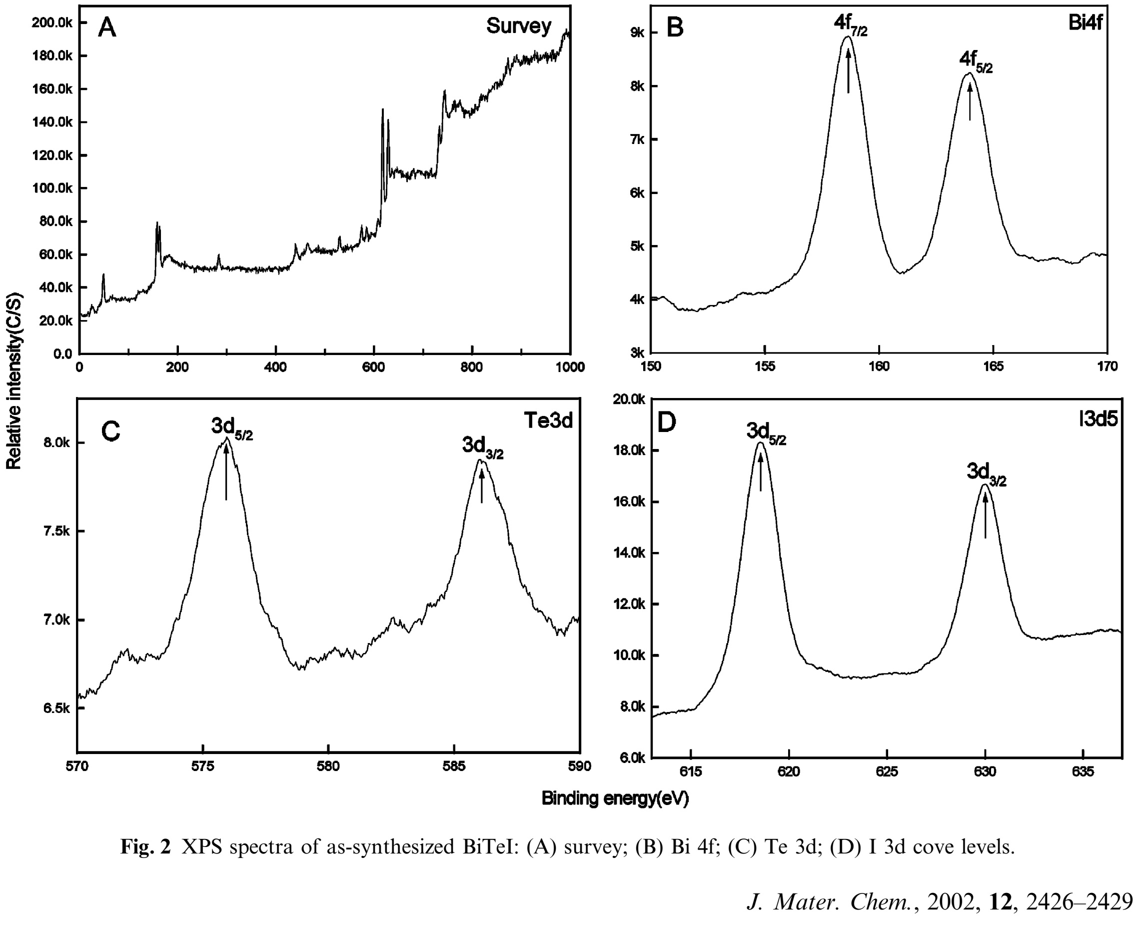

Fig. 2 XPS spectra of as-synthesized BiTeI: (A) survey; (B) Bi 4f; (C) Te 3d; (D) I 3d cove levels.

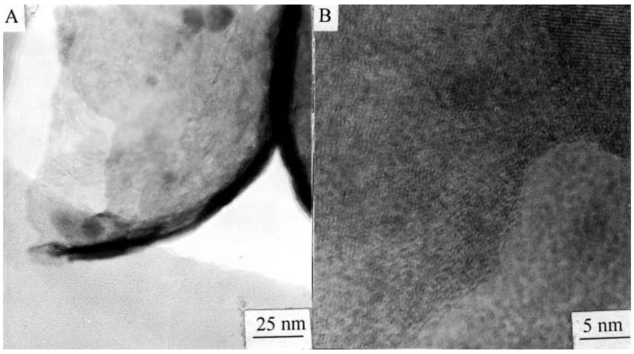

Fig. 4 HRTEM images of as-prepared BiTeI spheres: (A) a broken sphere; (B) higher magnification image of the sphere wall.

formation BiTeI submicrometer hollow spheres. The optimum reaction temperature is 190–200 °C. When the temperature is lower than 190 °C, the yield of BiTeI submicrometer hollow spheres decreases. The spheres are very sensitive to beam irradiation during TEM examination, which is presumably due to their thin walls. Higher reaction temperatures (such as 220 °C) are not beneficial for the formation of BiTeI hollow spheres because the iodine not only plays a transport role, but can also accelerate the reaction (eqn. 3).[29] When the starting materials Bi_2Te_3 and iodine are added to the autoclave in the molar ratio 1 : 1, the final product is Bi_2Te_3. In the hydrothermal process, the pH of the reaction system slightly changes, indicating that iodine does not undergo the disproportionation reaction (eqn. 1) and only dissolves in the water. When the molar ratio of Bi_2Te_3 to iodine is greater than 1 : 5, the obtained BiTeI shows hollow sphere morphology. In the hydrothermal process, the initial pH of the starting materials is about 7, but the pH of the reaction system is less than 1 after the reaction is completed. This demonstrates that iodine not only dissolve in the water, but also initiates the disproportionation reaction and produces HI, which reacts with Bi_2Te_3 nanocrystallites (eqn. 3) and produces BiTeI. Bruibsma *et al.* also reports that the pH of a reaction system changes when synthesizing hollow structures.[12]

A possible growth mechanism for the BiTeI hollow spheres will now be proposed, a schematic illustration of which is shown in Fig. 5. In the hydrothermal system, HI produced from the iodine disproportionation reaction encircles laminar Bi_2Te_3 oriented on the (001) plane.[30] A small amount of laminar BiTeI is formed *via* the reaction between HI and Bi_2Te_3 (see eqn. 3) on the surface of the laminar Bi_2Te_3. Because the lattice constant of BiTeI (a = 4.344 Å) is very close to that of Bi_2Te_3 (a = 4.384 Å) and BiTeI exhibits a CdI_2-type structure (the bonds between the layers are weak and thought to be of the van der Waals type[19,20]), the little BiTeI flakes attach themselves to both sides of the Bi_2Te_3 flakes. The BiTeI flakes attached to the Bi_2Te_3 gradually swell up like a balloon being inflated as HI diffuses to the inside of the flakes and H_2Te (see eqn. 3 and Fig. 5) diffuses to the outside. The matchable lattices as well as the equilibrium between the surface energy and the interface energy of the "balloon" may result in a sphere being formed.

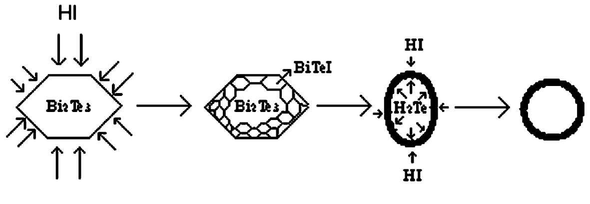

Fig. 5 Schematic illustration of the possible growth mechanism for BiTeI hollow spheres.

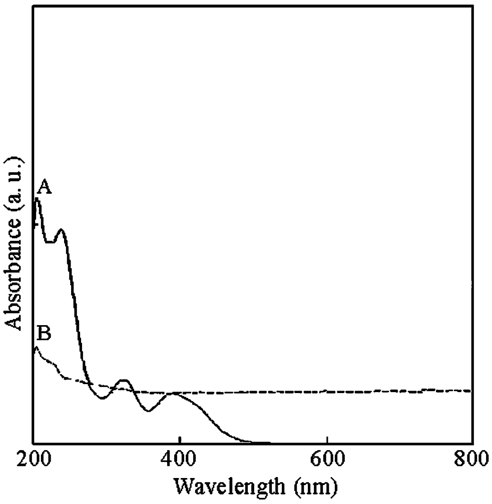

Fig. 6 UV-vis absorption spectra of (A) BiTeI and (B) Bi_2Te_3 at room temperature.

Fig. 6 shows the UV-vis absorption spectra of BiTeI and Bi_2Te_3 dispersed in absolute ethanol at room temperature. The absorption spectrum of the BiTeI submicrometre hollow spheres shows well-resolved peaks and is very similar to that of layered iodide compounds in colloidal solutions.[31] In BiTeI, the corrugated $(BiTe)^+$ layers have a geometry resembling that of the bismuth layers in metallic bismuth. According to a semi-ionic model, bismuth and tellurium atoms form positively charged $(BiTe)^+$ layers, while bismuth–iodine contacts are considered to be ionic.[20] According to the assignment of the absorption bands in Bi^{3+} ions,[32] the well-resolved peaks in Fig. 6(A) may be ascribed to transitions from the $^1S_0$ to $^3P_1$, $^3P_2$and $^1P_1$ states, respectively. The transition from $^1S_0$ to $^3P_2$ is forbidden in free Bi^{3+} ions, but may allowed in BiTeI because the symmetry of the "Bi^{3+}" ion is lowered by the surrounding three tellurium and three iodine atoms.[19] The first excitonic peak[31] at 380 nm (3.26 eV), with the band gap $\approx$ 2.25 eV (estimated from the absorption onset[33]), is considerably blue shifted in comparison with the band gap of the bulk materials,[16,17] an observation which may be attributed to quantum confinement effects.

IV Conclusion

In summary, BiTeI submicrometer hollow spheres have been successfully synthesized by an iodine transport hydrothermal method. A possible growth mechanism for the hollow structure has been proposed. The first exciton peak is considerably blue shifted in comparison with the band gap of the bulk materials as a result of quantum confinement effects. Compared with previous methods of preparing hollow spheres,[8–12] the method we describe here is simple in operation and requires no template materials[8–10] or surfactant (such as ref. 14*b*). A deeper understanding of the growth mechanism for the BiTeI hollow spheres, controlling the reaction kinetics and forming the monodispersed hollow spheres, is clearly needed.

Acknowledgement

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